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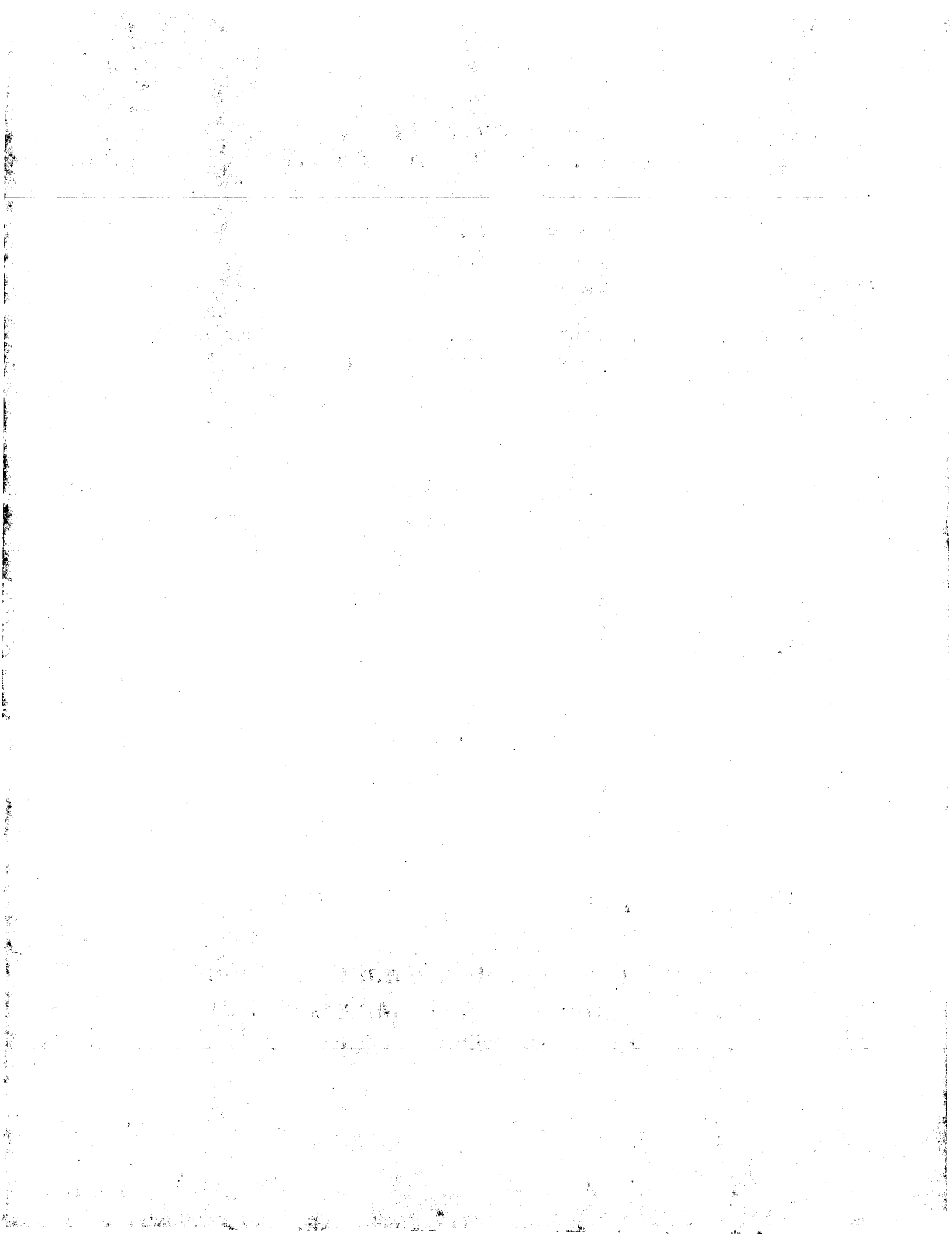
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(54) **Perfume-containing carrier having surface-modified particles for detergent composition**

(57) A perfume-containing carrier is provided for use in admixture with a particulate laundry detergent composition or as an additive to the wash solution separate from the detergent composition to impart a pleasing fragrance to laundered fabrics. The perfume-containing carrier comprises (i) discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume, the said perfume being adsorbed or absorbed or adsorbed and absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound i.e. a primary, secondary or tertiary amines or their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the fabric-adhesive agent being in contact with the particles and forming at least a partial coating on the surface, the perfume-containing carrier containing less than 5%, of surface active detergent compounds other than cationics.

## SPECIFICATION

**Perfume-containing carrier having surface-modified particles for laundry composition**

- 5 The present invention relates to perfume-containing carriers which significantly enhance the substantivity of perfume to laundered fabrics. More particularly, this invention relates to particulate detergent compositions which include as a component thereof a perfume-containing carrier which is able to impart a pleasing perfume fragrance to the finished laundered fabrics with only minimal amounts of perfume. 5
- 10 The present application is related to copending U.S. Application Serial No. 499,926 filed on 1st June, 1983, which corresponds to G.B. Application No. which claims priority therefrom under the International Convention, which describes a perfume-containing carrier comprising discrete particles containing a clay mineral (other than talc) and/or a zeolite; and a perfume. 10
- 15 Perfume substances which modify or enhance the aroma of detergent compositions or impart a pleasing aroma thereto are well-known in the art. U.S. Patent No. 4,131,555 and 4,228,026, are illustrative of patents which describe substances intended to impart a pleasing aroma or fragrance to liquid and granular detergent compositions. The described methods of preparation consist of mixing the perfume substances, in solid form, with the prepared detergent 20 compositions to form a homogeneous composition. Perfumes which are in liquid form are conventionally added to liquid detergent compositions as a component thereof or sprayed upon the surface of granular detergent compositions. However, detergent compositions which are thus prepared are unable to impart a perfume fragrance to the fabrics being laundered notwithstanding the enhanced aroma of the composition itself. Primarily, this is because the perfume 25 substances in the detergent composition are rapidly dispersed and diluted during laundering in the aqueous wash solution along with the water-soluble components of the detergent composition. Consequently, only a relatively minor amount of the perfume is available to contact and adhere to the fabric being laundered, the major portion of the perfume being drained from the washing machine with the wash solution during the wash cycle. Moreover, to the extent that 30 some perfume is still in contact with the fabric after the washing operation, it tends to be dissipated subsequently during drying, such as, for example, in a gas or electric dryer in which the washed fabrics are tumbled at relatively high temperatures. As a result, fabrics laundered with conventional detergent compositions generally retain only a very faint perfume fragrance which has no particular aesthetic appeal to the user. There is, therefore, a need in the art for an additive to conventional detergent compositions which can effectively provide a perfume 35 fragrance to fabrics being laundered such that the finished laundered fabrics have added appeal to the user.
- U.S. Patent No. 4,259,373 discloses a fabric conditioning article for use in an automatic washer or dryer consisting of a sealed water-insoluble pouch containing what is described as a 40 softener/antistat composition. In Example II of that specification, there is described a preparation procedure for such antistat composition wherein clay and solid perfume are mixed and the mixture then blended with sprayed particles of certain quaternary ammonium salts. The resulting composition is then filled into a sealed polyester pouch.
- Included among the perfume-containing carriers of the invention described is a particular 45 embodiment which comprises a perfume, particles of clay and a quaternary ammonium compound (sometimes referred to herein as a "QA" compound for convenience). Compositions containing clay and QA compounds are broadly described in the art relating to fabric softeners and anti-stat compositions. U.S. Patent No. 3,886,075, for example, describes a composition containing a smectite clay, a water-soluble QA compound and an "amino compatibilizing 50 agent" which is said to provide fabric softening and anti-static effects. U.S. Published Patent Application No. B305,417 describes a granular laundering composition comprising a soap-based granule, a smectite-type clay and a quaternary ammonium antistatic agent. In U.S. Patent No. 3,862,058, a clay and a quaternary ammonium compound are added to a non-soap synthetic detergent compound to provide a granular laundry detergent composition. U.S. 55 Patent Nos. 3,993,573 and 3,954,632 describe fabric softening compositions containing the aforementioned clay and QA compounds in combination with a so-called "acid compatibilizing agent". U.S. Patent No. 4,292,035 discloses a softening composition comprising smectite clay; an amine or quaternary ammonium compound as a softening agent; and an anionic surfactant wherein the fabric softening agent is reacted with the clay to form an "organo-clay complex" 60 prior to the addition of the anionic surfactant.
- The methods described in the art for preparing the aforementioned fabric softening compositions are characterised by either a deposition of QA compound upon granules composed of a uniform blend of clay with detergent and other ingredients (rather than a preferential deposition upon clay granules) or alternatively, the QA compound is reacted with the clay to provide a 65 modified clay in which preferably from about 10 to about 60 molar percent of the exchangeable

cations are alkyl substituted ammonium ions. Thus, for example, U.S. Patent Nos. 3,862,058 and 3,886,075 describe a method of preparation whereby the clay is initially admixed in a crutcher with the detergent, builder and other ingredients of the laundering compositions and the resulting mixture then spray-dried to form granules. The QA compound is thereafter sprayed upon the granules from a melt, it being a critical aspect of the method of preparation to avoid spraying the detergent granules with an aqueous solution or suspension of the QA compound. United States Published Patent Application B305,417 discloses a method of preparation wherein clay is mixed with soap-based granules in a drum mixer. The QA compound is then added to the resulting composition by spraying from a melt. U.S. Patent No. 3,594,212 describes a method of softening fibrous materials wherein such materials are successively impregnated with an aqueous dispersion of clay and an aqueous solution of QA compound, the amount of QA compound in solution being sufficient to effect at least a partial cation exchange with the clay retained on the fibrous material. In U.S. Patent No. 3,948,790 to Speakman, there is described a procedure for preparing "quaternary ammonium clays" whereby a QA compound is reacted with clay by slurring the untreated clay in a solution containing the desired quantity of QA compound. The QA compounds which may be thus employed are said to be restricted to short-chain compounds having a maximum of four carbon atoms per chain, the total number of carbon atoms in the compound not exceeding eight. The quantity of such QA compound added to the solution is controlled so as to provide the desired degree of ion exchange with the clay. The examples of the patent describe various treated clays in which from about 5 to 40% of the exchangeable cations are replaced by quaternary ammonium cations, the amount of QA compound in solution being necessarily restricted to that which is required to effect a partial exchange reaction with the clay. Accordingly, the prior art does not contemplate the particular combination of clay particle and QA compound employed in the present invention, much less contemplate using such combination as a carrier for perfume in accordance with the present invention.

The present invention provides an improved perfume-containing carrier comprising: (i) discrete particles containing at least 75%, by weight, of a clay mineral (other than talc) and/or a zeolite; (ii) a perfume, the said perfume being adsorbed and/or absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of detergent compounds other than cationic detergents.

In accordance with process aspect of the invention, the deposition of perfume on laundered fabrics is effected by contacting the stained and/or soiled materials to be laundered with an aqueous solution or dispersion which contains the above-defined perfume-containing carriers.

40 The term "perfume", as used herein refers to odouriferous materials which are able to provide a pleasing fragrance to fabrics, and encompasses conventional materials commonly used in detergent compositions to counteract a maldour in such compositions and/or provide a pleasing fragrance thereto. The perfumes are preferably in the liquid state at ambient temperature, although solid perfumes are also useful. Included among the perfumes contemplated for use herein are materials such as aldehydes, ketones, esters and the like which are conventionally employed to impart a pleasing fragrance to liquid and granular detergent compositions. Naturally occurring plant and animal oils are also commonly used as components of perfumes. Accordingly, the perfumes useful for the present invention may have relatively simple compositions or may comprise complex mixtures of natural and synthetic chemical components, all of which are intended to provide a pleasant odour or fragrance when applied to fabrics. The perfumes used in detergent compositions are generally selected to meet normal requirements of odour, stability, price and commercial availability. A description of the materials conventionally used in detergent perfumery is set forth by R. T. Steltenkamp, *The Journal of the American Oil Chemists Society*, Vol. 45, No. 6, pp. 429-432, such disclosure being incorporated herein by reference.

55 The term "particles" as used throughout the specification and claims with regard to the perfume-containing carrier is intended to encompass a wide variety of particulate matter of differing shape, chemical composition, particle size and physical characteristics, the essential common characteristic being that such particles contain at least 75%, by weight, of a clay mineral or a zeolite or a mixture thereof. The particles are desirably free-flowing in nature. The "weight percent" of the clay mineral and the zeolite refers to the weight of such materials including the water and impurities associated with the particular clay or zeolite employed. Accordingly, the carrier particles may be in the form of finely divided powders, as well as relatively larger-sized granules beads or agglomerated particles, and may be produced by diverse methods of manufacture such as spray-drying, dry-blending or agglomeration of individual

components. Particularly preferred carrier particles for use herein are bentonite agglomerates produced by the method described in USSN 366,587, filed 8th April, 1982, which corresponds to G.B. Application No. 83.09605 (published as 2121843A), the disclosure of which is incorporated herein by reference. The carrier particles may thus optionally include in addition to the clay mineral and/or zeolite, materials which are compatible with conventional laundering compositions, examples of suitable materials including binding or agglomerating agents, e.g. sodium silicate, dispersing agents, detergent builder salts, filler salts as well as common minor ingredients present in conventional laundry detergent compositions such as dyes, optical brighteners, anti-redeposition agents and the like. For the purposes of the present invention, the particles should contain less than about 5%, by weight, of surface active detergent compounds, preferably less than about 3%, by weight, and most preferably are substantially free of surfactants.

The term "discrete" as used herein with regard to the particles refers to the fact that such particles are employed in the present invention as individually distinct particles, thus excluding, for example, carrier particles which are encompassed within a matrix of other materials, or which are blended with other ingredients such that the particles become a component of a larger aggregate material rather than being in the form of individual and distinct particles.

The present invention is characterised by an effective perfume-containing carrier wherein the carrier particles contain at least 75%, by weight, preferably at least 90%, by weight, of a clay mineral other than talc and/or a zeolite. The major portion of the perfume associated with the carrier, preferably at least 95% thereof, is adsorbed and/or absorbed on the said particles, the terms "adsorbed" and "absorbed" being used herein to refer to the physical association of the perfume with the carrier particles. Unlike conventional practice wherein the perfumes added to granular detergent compositions are sprayed upon or otherwise contacted with the water-soluble spray-dried granular powders, the perfumes employed in the present invention are contacted with particles of a clay mineral or zeolite which are, for the most part, water-insoluble. It has been found that the perfume thus associated with the carrier particles remains primarily concentrated upon such particles during laundering rather than being dispersed in the aqueous wash solution. This provides a significant advantage during laundering insofar as the perfume-containing carrier particles in the wash solution are likely to contact the laundered fabrics and be dispersed thereupon, particularly in a washing machine where the wash solution is mechanically drained through the fabric during the wash cycle. The perfume is thus maintained proximate to the finished laundered fabric, preventing the dissipation of the perfume fragrance from such fabrics.

Moreover, retention of the carrier particles upon the surface of the laundered fabrics is enhanced by the fabric adhesive agent which forms at least a partial coating upon the surface of the particles. Thus, for example, the use of an anionic or nonionic surfactant as a fabric adhesive agent in accordance with the present invention provides a pasty adhesive-like surface to the carrier particles, increasing the likelihood of such particles being entrapped upon the fabrics during laundering. The use of a cationic compound similarly enhances fabric adhesion, albeit in a different manner. Although applicants do not wish to be bound to a particular theory of operation, it is believed that the deposition of a cationic compound upon the surface of the particles imparts a positive surface charge to such particles which creates a driving force for the positively charged particles to attach themselves to the negatively charged surface of the fabrics being laundered, and particularly, to fabrics containing substantial amounts of cotton. Furthermore, the surface modified particles of clay or zeolite are generally hydrophobic in nature, the clay itself being hydrophilic. The hydrophobicity of the particles is particularly advantageous in hand-wash laundering operations because the hydrophobic particles are not as readily dispersible in the aqueous hand-wash solution as untreated particles and, therefore, tend to remain upon the surface of the wash solution for longer periods of time. This has the effect of enhancing the availability of such particles for contact with and deposition upon the fabrics being laundered, thereby increasing the likelihood of maintaining the desired perfume fragrance in the hand-washed fabrics.

The perfume-containing carriers of the present invention are comprised of three essential ingredients: a clay mineral and/or a zeolite, a perfume; and a defined fabric-adhesive agent. The weight ratio of clay mineral or zeolite to perfume in the carriers is generally from about 10:1 to about 200:1 and preferably from about 20:1 to about 100:1. The weight of perfume in the carrier will generally vary within the range of from about 0.2 to 10%, and preferably from about 0.5 to 5%, by weight, thereof. The carriers may be conveniently employed during home laundering as additives to a laundry washing bath separate from the detergent composition, such as, for example, a rinse-cycle additive or alternatively, the carriers may be incorporated into a conventional laundry detergent composition as a component thereof. Such fully-formulated detergent compositions generally comprise (a) from about 0.1 to about 50%, by weight, preferably from about 5 to about 30%, by weight, of the said perfume-containing carrier; and (b) from about 2 to about 50%, by weight preferably from about 5 to about 40%, by weight,

- and most preferably from about 5 to about 30%, by weight, of a surface active agent selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergents, the amount of such detergents being additional to any detergent compound in the perfume-containing carrier. The detergent compositions optionally also contain from 0 to about 70%, by weight, of a detergent builder salt, a concentration of from about 5 to about 50% being particularly preferred. The balance of the composition will predominantly comprise water, filler salts, such as, sodium sulphate, and optionally minor components such as binders, optical brighteners, pigments, dyes and the like which are conventional adjunct materials in detergent formulations.
- For purposes of economy it is preferred that the major portion, and in most instances, preferably substantially all, of the perfume contained in the detergent composition be provided by the carriers. However, the detergent compositions useful herein may also include perfumes additional to that employed in conjunction with the above-described carriers to provide a pleasant odour to the wash solution or to the composition itself. The use of additional perfumes may also be advantageous in instances where it is used in conjunction with a limited amount of a more expensive perfume. Thus, for example, it may be economically desirable to utilize a minor amount of a relatively expensive perfume with the carrier of the invention and provide relatively larger amounts of a less expensive perfume to the granular detergent composition as a supplementary fragrance, the latter perfume being added by techniques known in the art, such as, by spraying the granular detergent powder.
- The clay minerals which are generally useful herein include a wide variety of materials included among which are smectite-type clays; kaolinite, metakaolin; and attapulgite. Of the above-mentioned types of clay minerals, the smectite-type clays are preferred because they advantageously provide desirable softening effects to the laundered fabrics in addition to serving as a carrier for perfume in accordance with the present invention. A detailed description of the various types of clay minerals, all of which may be used in the present invention, is set forth by B.K.G. Theng, *The Chemistry of Clay Organic Reactions*, John Wiley & Sons, (1974) pp. 1-15, such disclosure being incorporated herein by reference.
- The crystalline types of zeolite which may be employed herein include those described in "Zeolite Molecular Sieves" by Donald W. Breck, published in 1974 by John Wiley & Sons, typical commercially available zeolites being listed in Table 9.6 at pages 747-749 of the text, such table being incorporated herein by reference. Zeolite structures of type A are especially desirable and are extensively described in the art; see, for example, page 133 of the aforementioned Breck text as well as U.S. Patent No. 2,882,243. Type 4A zeolite is advantageously employed, the univalent cation of such zeolite being sodium and the pore size of the zeolite being about 4 Angstroms.
- The aforementioned smectite-type clays are three-layer clays characterised by the ability of the layered structure to increase its volume several-fold by swelling or expanding when in the presence of water to form a thixotropic gelatinous substance. There are two classes of smectite-type clays: in the first class, aluminium oxide is present in the silicate crystal lattice; in the second class, magnesium oxide is present in the silicate crystal lattice. Atom substitution by iron, magnesium, sodium, potassium, calcium and the like can occur within the crystal lattice of the smectite clays. It is customary to distinguish between clays on the basis of their predominant cation. For example, a sodium clay is one in which the cation is predominantly sodium. With regard to the present carriers, aluminium silicates wherein sodium is the predominant cation are preferred, such as, for example, bentonite clays. Among the bentonite clays, those from Wyoming (generally referred to as western or Wyoming bentonite) are especially preferred.
- Preferred swelling bentonites are sold under the trademark Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark THIXO-JEL, are selectively mined and beneficiated bentonites, and those considered to be most useful are available as Mineral Colloid No's 101, etc. corresponding to THIXO-JEL's No's. 1, 2, 3 and 4. Such materials have pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the pulverized grade at least about 85% (and preferably 100%) passes through a 200 mesh U.S. Sieve Series sieve (which has openings 74 microns across). More preferable, the bentonite is one wherein essentially all the particles (i.e. at least 90% thereof, preferably over 95%) pass through a No. 325 sieve (U.S. Sieve Series) (which has openings 44 microns across) and most preferably all the particles pass through such a sieve. The swelling capacity of the bentonites in water is usually in the range of 3 to 15 ml/gram, and its viscosity, at a 6% concentration in water, is usually from about 8 to 30 centipoises.
- In a particularly preferred embodiment of the invention, the carrier particles comprise agglomerates of finely divided bentonite, of particle sizes less than No. 200 sieve, agglomerated to particles of sizes essentially in the No's. 10-100 sieve range (U.S. Sieve series) (which have openings 2000 to 149 microns across), of a bulk density in the range of 0.7 to 0.9 g/ml and a

moisture content of 8 to 13%. Such agglomerates include about 1 to 5% of a binder or agglomerating agent to assist in maintaining the integrity of the agglomerates until they are added to water, in which it is intended that they disintegrate and disperse. A detailed description of the method of preparation of such agglomerates is set forth in the aforementioned U.S. Serial No. 366,587, filed 8th April, 1982 which corresponds to G.B. Application No. 83.09605 (published as 2121843A) which is incorporated herein by reference.

Instead of utilizing the THIXO-JEL or Mineral Colloid bentonites one may employ products, such as that sold by American Colloid Company, Industrial Division, as General Purpose Bentonite Powder, 325 mesh, which has a minimum of 95% thereof finer than 325 mesh or 44 microns in diameter (wet particle size) and a minimum of 96% finer than 200 mesh or 74 microns diameter (dry particle size). Such a hydrous aluminium silicate is comprised principally of montmorillonite (90% minimum), with smaller proportions of feldspar, biotite and selenite. A typical analysis, on an "anhydrous" basis, is 63.0% silica, 21.5% alumina, 3.3% of ferric iron (as  $\text{Fe}_2\text{O}_3$ ), 0.4% of ferrous iron (as  $\text{FeO}$ ), 2.7% of magnesium (as  $\text{MgO}$ ), 2.6% of sodium and potassium (as  $\text{Na}_2\text{O}$ ), 0.7% of calcium (as  $\text{CaO}$ ), 5.6% of crystal water (as  $\text{H}_2\text{O}$ ) and 0.7% of trace elements.

Although the western bentonites are preferred it is also possible to utilize other bentonites, such as those which may be made by treating Italian or similar bentonites containing relatively small proportions of exchangeable monovalent metals (sodium and potassium) with alkaline materials, such as sodium carbonate, to increase the cation exchange capacities of such products. It is considered that the  $\text{Na}_2\text{O}$  content of the bentonite should be at least about 0.5%, preferably at least 1% and more preferably at least 2% so that the clay will be satisfactorily swelling, with good softening and dispersing properties in aqueous suspension. Preferred swelling bentonites of the types described above are sold under the trade names Laviosa and Winkelman, e.g. Laviosa AGB and Winkelman G-13.

The silicate, which may be employed as a binder to hold together the finely divided bentonite particles in agglomerated form, is preferably a sodium silicate of  $\text{Na}_2\text{O}:\text{SiO}_2$  e.g. 1:2.4. The silicate is water soluble and solutions thereof at concentrations up to about 50%, by weight, may be employed in the preparation of the aforementioned bentonite agglomerates, all of such solutions being free flowing, especially at the elevated temperatures to which the silicate solution is preferably heated during the preparation procedure.

The cationic compounds are employed as fabric adhesive agents in the carriers of the present invention in an amount of from about 0.2 to about 16%, and preferably from about 1 to 5%, by weight. In the fully-formulated detergent compositions of the present invention, the cationic compounds are present in an amount of from about 0.01 to about 10%, more usually from about 0.05 to 2%, and preferably from about 0.1 to 1%, by weight. When the fabric-adhesive agent is comprised exclusively of an anionic or nonionic detergent compound, such detergent is present in the carriers in an amount from about 0.2 to less than 5%, by weight, and preferably from about 1 to below 5%, by weight.

The useful primary, secondary and tertiary amines and their water-soluble salts are generally of the formula  $\text{R}^1\text{R}^2\text{R}^3\text{N}$ , wherein  $\text{R}^1$  represents an alkyl or alkenyl group containing from about 8 to 22 carbon atoms and  $\text{R}^2$  and  $\text{R}^3$  each represent hydrogen or hydrocarbyl groups containing from 1 to 22 carbon atoms, the term "hydrocarbyl group" encompassing alkyl, alkenyl, aryl and alkaryl groups including substituted groups of this type, common substituents being hydroxy and alkoxy groups.

Within the general description of amines given above, specific examples include primary tallow amine, primary coconut amine, secondary tallow methyl amine, tallow dimethyl amine, tritallow amine, primary tallow amine hydrochloride, and primary coconut amine hydrochloride.

The useful diamine and diammonium salts have the general formulas:  $\text{R}^1\text{R}^2\text{NR}^5\text{NR}^3\text{R}^4$ ;  $[\text{R}^1\text{R}^2\text{NR}^5\text{NR}^3\text{R}^4\text{R}^6]^+\text{X}^-$ ;  $[\text{R}^1\text{R}^2\text{R}^3\text{NR}^5\text{NR}^4\text{R}^6]^+\text{X}^-$ ;  $[\text{R}^1\text{R}^2\text{R}^3\text{NR}^5\text{NR}^4\text{R}^6\text{R}^7]^+\text{X}^-$ ; wherein  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are as defined above,  $\text{R}^4$ ,  $\text{R}^6$  and  $\text{R}^7$  have the same definition as  $\text{R}^2$  and  $\text{R}^3$ , and  $\text{R}^5$  represents an alkylene chain having from 4 to 6 carbon atoms wherein the middle carbon atoms may be linked to each other by an ether oxygen or by a double or triple bond.  $\text{X}^-$  represents an anion, preferably chloride, bromide, sulphate, methyl sulphate or similar anion.

Specific examples of diamines and diamine salts include N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N-tallow-1,3-diaminopropane dioleate and N-tallow-1,3-diaminopropane diacetate.

Also suitable for use herein are the ethoxylated amine and diamine salts with fatty alkyl groups of coconut, tallow and stearyl and containing from about 2 to 50 moles of ethylene oxide.

The useful quaternary ammonium compounds are generally of the formula  $[\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}]^+\text{X}^-$ , wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{X}$  are as defined above,  $\text{R}^4$  represents an organic radical selected from among those defined for  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ . Although not indicated in the above formula,  $\text{R}^1$  and/or  $\text{R}^4$  may be attached to the quaternary nitrogen atom through an ether, alkoxy, ester or amide



linkage. Among the quaternary ammonium compounds known to add substantivity to fabrics, particularly fabrics containing substantial amounts of cotton, three basic types are particularly useful for the present invention: (1) alkyl dimethyl ammonium compounds; (2) amido alkoxy-  
5 description of these three types of compounds is set forth by R. Egan in *Journal American Oil Chemists' Society*, January, 1978 (Vol. 55), pages 118-121, such disclosure being incorporated herein by reference. 5

Long chain quaternary ammonium compounds are generally preferred for use herein, namely, compounds wherein the number of carbon atoms is greater than eight. Within the more general  
10 description provided above concerning quaternary ammonium compounds useful for the present invention, preferred specific quaternary ammonium compounds include di-hydrogenated tallow dimethyl ammonium methyl sulphate; di-hydrogenated tallow dimethyl ammonium chloride, and 1-methyl-1-alkylamidoethyl-2-alkylimidazolinium methyl sulphate wherein the "alkyl groups" are  
15 benzyl quaternary compounds that are useful include those wherein the alkyl group is of a mixture of alkyl groups of 10 to 18 carbon atoms or 12 to 16 carbon atoms, e.g. lauryl, myristyl and palmityl. The various materials mentioned above are available commercially from various manufacturers, those from Sherex Chemical Company being identified by tradenames such as Adogen; Arosurf; Variquat; and Varisoft. 15

20 The quaternary ammonium salts employed herein are preferably substantially free of a conductive salt; the term "conductive salt" being used herein to refer to salts which are electrically conductive in aqueous solution. The conductive salts generally have a cation anion-bond of at least 50% ionic character as calculated in accordance with the method described in Pauling, "The Nature of the Chemical Bond", 3rd Edition, 1960. By use of the term  
25 "substantially free" is meant a concentration of conductive salt less than that present at normal impurity levels in the quaternary ammonium compound. Generally, the concentration of conductive salt is below 1%, by weight. 25

The perfume-containing carriers of the invention are prepared by methods wherein the carrier particles are initially contacted with the perfume to be employed such that the major portion,  
30 preferably substantially all, of such perfume is adsorbed and/or absorbed by such particles. The resulting perfume-containing particles are then contacted with the fabric adhesive agent such that substantially all of such fabric adhesive agent is adsorbed upon the surface of the particles and forms at least a partial coating thereupon. 30

A preferred technique for contacting the carrier particles with perfume consists of spraying the  
35 perfume upon the surface of the particles. This may be effected, for example, by spraying the perfume from a pressurized nozzle so as to produce droplets which contact the surface of the particles, the latter being conveniently on a moving belt, such as, a conveyor belt. Alternatively, the process may be conveniently carried out by spraying the perfume over particles which are contained in a rotary drum or tube inclined at a slight angle, such as, from about 5° to 15°, the  
40 rotational speed of such drum or tube being suitably from about 5 to 100 rpm. The range of suitable droplet size for effective spraying may vary from about 10 to about 200 microns in diameter, but preferably should be as small as possible relative to the diameter of the particles being sprayed. 40

The step of contacting the clay particles with the fabric adhesive agent may be carried out  
45 using the same methods described above with regard to perfume sorption upon the carrier particles. Thus, for example, a solution or suspension of an anionic or nonionic detergent compound may be sprayed upon the surface of the particles to form a coating thereon. Where the fabric adhesive agent is a cationic compound, and the carrier particles comprise a clay mineral such as a smectite clay, it is important that the deposition of such compound is effected  
50 under conditions which minimize the likelihood of an ion exchange reaction between the clay and the cationic compound. Accordingly, the method of contacting the clay mineral particles with a cationic compound is primarily concerned with avoiding the transformation of a major portion of the clay to a clay complex by an ion exchange reaction, thereby excluding, for example, the methods of preparing a "QA clay" and an "organo-clay complex" referred to in  
55 U.S. Patent Nos. 3,948,790 and 4,292,035, respectively. To promote the adsorption of a cationic compound upon the surface of the clay particles, process conditions which favour swelling of the clay are generally avoided so as to minimize the likelihood of an undesired exchange reaction. Swelling of the clay is particularly favoured in an aqueous slurry, hence, the less water which contacts the clay, the less the likelihood of effecting a cation exchange  
60 reaction. Accordingly, the weight of aqueous solvent which contacts the clay is generally restricted to an amount less than the weight of the clay, preferably below 50%, and more preferably below 25%, by weight, of such clay. 60

A preferred method of preparation comprises spraying the surface of the clay particles with a substantially non-aqueous solution or suspension containing the cationic compound, the  
65 concentration of water in such solution or suspension being maintained generally below about 65

50%, by weight, and preferably below about 10%, by weight. This is conveniently effected by spraying the solution or suspension of cationic compounds from a pressurized nozzle as described above. Spraying is preferably carried out at ambient temperatures and generally below 100°F (38°C). At temperatures above 100°F (38°C), particularly above 140°F (60°C), the

5 cationic compounds may be undesirably absorbed into the clay particles. Any organic solvent in which the cationic compound can be dispersed may be conveniently employed to form a solution or suspension for contacting the clay particle. Useful solvents include propylene glycol, hexylene glycol, ethanol and isopropyl alcohol. 5

In an alternative process of preparation, the particles of clay mineral or zeolite are placed on a vibrating conveyor belt which is continuously wetted with a solution or suspension of a cationic compound, the effect of the vibration being to impart at least a partial coating of the cationic solution or suspension upon the surface of the particles. 10

In accordance with another embodiment of the present invention, finely divided particles as described above are bonded to the surface of a granular detergent composition which is devoid of a soap to form agglomerate particles consisting of detergent-base granules encapsulated within a surface coating of a clay mineral. The agglomerate particles are characterised by an inner portion consisting of the detergent-base granules, and a surface portion contacting and surrounding such inner portion consisting essentially of particles containing at least about 75%, by weight, and preferably greater than about 90%, by weight, of a clay mineral and/or a zeolite and less than about 5%, by weight, of surface active detergent compounds other than cationic detergents, preferably substantially free of such surfactants. 15 20

To achieve a substantially continuous external surface of the clay mineral on the agglomerate particles, the carrier particles employed are as small as possible relative to the detergent-base granules, allowing the particles to be closely packed around the granules. The detergent composition granules are preferably spray-dried particles having sizes within mesh Nos. 8 to 100, U.S. Sieve Series (which have openings 2380 to 149 microns across). The carrier particles are preferably sufficiently small that they pass through a No. 325 mesh screen, U.S. Sieve Series (which has openings 44 microns across). The weight ratio of detergent composition granules to clay-containing particles may vary from about 10:1 to about 1:2, preferably from about 5:1 to 1:1. The application of the particles to the base detergent granules may be effected by standard agglomeration techniques and equipment. One method that has been found to be especially useful is to mix the desired weights of the detergent composition granules and finely divided clay powder and while mixing, spray water on to the moving surfaces thereof, or more preferably, spray a dilute sodium silicate solution. Spraying may be carried out at room temperature and should be gradual enough so as to prevent any objectionable lumping of the mixture. Mixing will continue in this manner until the clay particles all adhere to the detergent-base granules, after which mixing may be halted and the product may be screened or otherwise classified to be within the desired product size range. The silicate solution employed is normally at a concentration of about 0.05 to 10%, by weight, typically from about 1 to 6%, by weight. 25 30 35 40 45

The amount of silicate solution applied to the detergent-base granules generally constitutes from about 0.01 to about 2%, by weight. Satisfactory agglomeration and surface coating are obtained at such concentration using suitable agglomerating equipment, such as an O'Brien agglomerator, or a conventional inclined drum equipped with spray nozzles and baffles. The silicate concentration should not be so high as to inhibit dispersion of the softening particles in the wash solution when the product is employed in laundry operations. Although it is preferred that silicate be employed in the agglomerating spray, useful product is obtainable by utilizing water alone as an agglomerating or binding agent or by employing aqueous solutions of other binders, such as gum, resins and surface active agents.

The sorption of the fabric adhesive agent and perfume upon the surface of the agglomerate particle is carried out using the same methods described above with regard to the preparation of the carriers of the present invention. The resulting agglomerate particles are useful laundry products in which the detergent-base granule dissolves and functions in the standard manner in the wash solution while the particles of clay or zeolite become dispersed in the wash solution where they serve as perfume-containing carriers in accordance with the present invention. 50

55 The laundry detergent compositions with which the present perfume-containing carriers may be incorporated or with which it may be employed may contain one or more surface active agents selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergents. The synthetic organic detergents employed in the practice of the invention may be any of a wide variety of such compounds which are well known and are described at length in the text "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, the relevant disclosures of which are hereby incorporated by reference. 60

Among the anionic surface active agents useful in the present invention are those surface active compounds which contain an organic hydrophobic group containing from about 8 to 26 carbon atoms and preferably from about 10 to 18 carbon atoms in their molecular structure and 65

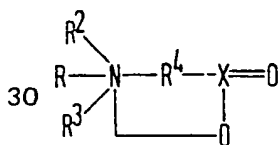
at least one water-solubilizing group selected from the group of sulphonate, sulphate, carboxylate, phosphonate and phosphate so as to form a water-soluble detergent.

- Examples of suitable anionic detergents include soaps, such as, the water-soluble salts (e.g. the sodium, potassium, ammonium and alkanolammonium salts) of higher fatty acids or resin salts containing from about 8 to 20 carbon atoms and preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, for example, tallow, grease, coconut oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, for example, sodium coconut soap and potassium tallow soap. 5
- The anionic class of detergents also includes the water-soluble sulphated and sulphonated detergents having an aliphatic, preferably an alkyl, radical containing from about 8 to 26, and preferably from about 12 to 22 carbon atoms. (The term "alkyl" includes the alkyl portion of the higher acyl radicals.) Examples of the sulphonated anionic detergents are the higher alkyl mononuclear aromatic sulphonates such as the higher alkyl benzene sulphonates containing from about 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, such as, for example, the sodium, potassium and ammonium salts of higher alkyl benzene sulphonates, higher alkyl toluene sulphonates and higher alkyl phenol sulphonates. 10
- Other suitable anionic detergents are the olefin sulphonates including long chain alkene sulphonates, long chain hydroxyalkane sulphonates or mixtures of alkene sulphonates and hydroxyalkane sulphonates. The olefin sulphonate detergents may be prepared in a conventional manner by the reaction of sulphur trioxide ( $\text{SO}_3$ ) with long chain olefins containing from about 8 to 25, and preferably from about 12 to 21 carbon atoms, such olefins having the formula  $\text{RCH}=\text{CHR}'$  wherein R represents a higher alkyl group of from about 6 to 23 carbons and R' represents an alkyl group containing from about 1 to 17 carbon atoms, or hydrogen to form a mixture of sultones and alkene sulphonic acids which is then treated to convert the sultones to sulphonates. Other examples of sulphate or sulphonate detergents are paraffin sulphonates containing from about 10 to 20 carbon atoms, and preferably from about 15 to 20 carbon atoms. The primary paraffin sulphonates are made by reacting long chain alpha olefins and bisulphites. Paraffin sulphonates having the sulphonate group distributed along the paraffin chain are shown in U.S. Nos. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent No. 735,096. 15
- Other suitable anionic detergents are sulphated ethoxylated higher fatty alcohols of the formula  $\text{RO}(\text{C}_2\text{H}_4\text{O})_m\text{SO}_3\text{M}$ , wherein R represents a fatty alkyl group of from 10 to 18 carbon atoms, m is from 2 to 6 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in the R group) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanolamino, or a higher alkyl benzene sulphonate wherein the higher alkyl group is of 10 to 15 carbon atoms. The proportion of ethylene oxide in the polyethoxylated higher alkanol sulphate is preferably 2 to 5 moles of ethylene oxide groups per mole of anionic detergent, with three moles being most preferred, especially when the higher alkanol is of 11 to 15 carbon atoms. To maintain the desired hydrophile-lipophile balance, when the carbon atom content of the alkyl chain is in the lower portion of the 10 to 18 carbon atom range, the ethylene oxide content of the detergent may be reduced to about two moles per mole whereas when the higher alkanol is of 16 to 18 carbon atoms in the higher part of the range, the number of ethylene oxide groups may be increased to 4 or 5 and in some cases to as high as 8 or 9. Similarly, the salt-forming cation may be altered to obtain the best solubility. It may be any suitably solubilizing metal or radical but will most frequently be an alkali metal, e.g. sodium, or ammonium. If lower alkylamine or alkanolamine groups are utilized the alkyl groups and alkanols will usually contain from 1 to 4 carbon atoms and the amines and alkanolamines may be mono-, di- and tri-substituted, as in monoethanolamine, di-isopropanolamine and trimethylamine. A preferred polyethoxylated alcohol sulphate detergent is available from Shell Chemical Company and is marketed as Neodol (Registered Trade Mark) 25-3S. 20
- The most highly preferred water-soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and tri-ethanolamine), alkali metal (such as, sodium and potassium) and alkaline earth metal (such as, calcium and magnesium) salts of the higher alkyl benzene sulphonates, olefin sulphonates and higher alkyl sulphates. Among the above-listed anionics, the most preferred are the sodium linear alkyl benzene sulphonates (LABS), and especially those wherein the alkyl group is a straight chain alkyl radical of 12 or 13 carbon atoms. 25
- The nonionic synthetic organic detergents are characterised by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to 30

achieve the desired balance between the hydrophobic and hydrophilic groups.

The nonionic detergent employed is preferably a poly-lower alkoxyated higher alkanol wherein the alkanol is of 10 to 18 carbon atoms and wherein the number of moles of lower alkylene oxide (of 2 or 3 carbon atoms) is from 3 to 12. Of such materials it is preferred to employ those wherein the higher alkanol is a higher fatty alcohol of 11 to 15 carbon atoms and which contain from 5 to 9 lower alkoxy groups per mole. Preferably, the lower alkoxy group is ethoxy but in some instances it may be desirably mixed with propoxy, the latter, if present, usually being a minor (less than 50%) constituent. Exemplary of such compounds are those wherein the alkanol is of 12 to 15 carbon atoms and which contain about 7 ethylene oxide groups per mole, e.g. Neodol (Registered Trade Mark) 25-7 and Neodol 23-6.5, which products are made by Shell Chemical Company, Inc. The former is a condensation product of a mixture of higher fatty alcohols averaging about 12 to 15 carbon atoms, with about 7 moles of ethylene oxide and the latter is a corresponding mixture wherein the carbon atom content of the higher fatty alcohol is 12 to 13 and the number of ethylene oxide groups per mole averages about 6.5. The higher alcohols are primary alkanols. Other examples of such detergents include Tergitol (Registered Trade Mark) 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corporation. The former is a mixed ethoxylation product of an 11 to 15 carbon atom linear secondary alkanol with seven moles of ethylene oxide and the latter is a similar product but with nine moles of ethylene oxide being reacted. Also useful in the present compositions are the higher molecular weight nonionic detergents, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products are also made by Shell Chemical Company.

Zwitterionic detergents such as the betaines and sulphobetaines having the following formula are also useful:



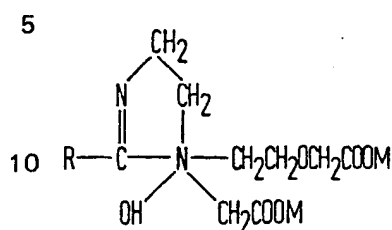
wherein R represents an alkyl group containing from about 8 to 18 carbon atoms, R<sup>2</sup> and R<sup>3</sup> each independently represent an alkyl or hydroxyalkyl group containing about 1 to 4 carbon atoms, R<sup>4</sup> represents an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms, and X represents a carbon atom or an S:O group. The alkyl group can contain one or more intermediate linkages such as amido, ether, or polyether linkages or nonfunctional substituents such as hydroxyl or halogen which do not substantially affect the hydrophobic character of the group. When X represents a carbon atom, the detergent is called a betaine; and when X represents an S:O group, the detergent is called a sulphobetaine or sultaine.

Cationic surface active agents may also be employed. They comprise surface active detergent compounds which contain an organic hydrophobic group which forms part of a cation when the compound is dissolved in water, and an anionic group. Typical cationic surface active agents are amine and quaternary ammonium compounds.

Examples of suitable synthetic cationic detergents include: normal primary amines of the formula RNH<sub>2</sub>, wherein R represents an alkyl group containing from about 12 to 15 atoms; diamines having the formula RNHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, wherein R represents an alkyl group containing from about 12 to 22 carbon atoms, such as N-2-aminoethyl-stearyl amine and N-2-amino-ethyl myristyl amine; amide-linked amines such as those having the formula R'CONHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, wherein R' represents an alkyl group containing about 8 to 20 carbon atoms, such as N-2-amino ethylstearyl amide and N-amino ethylmyristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group containing about 8 to 22 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate or methosulphate. The alkyl group may contain intermediate linkages such as amide which do not substantially affect the hydrophobic character of the group, for example, stearyl amido propyl quaternary ammonium chloride. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl-ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl-lauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulphates and acetates.

Ampholytic detergents are also suitable for the invention. Ampholytic detergents are well known in the art and many operable detergents of this class are disclosed by Schwartz, Perry

and Berch in the aforementioned "Surface Active Agents and Detergents". Examples of suitable amphoteric detergents include: alkyl betaminodipropionates,  $\text{RN}(\text{C}_2\text{H}_4\text{COOM})_2$ ; alkyl beta-amino propionates,  $\text{RN}(\text{H})\text{C}_2\text{H}_4\text{COOM}$ ; and long chain imidazole derivatives having the general formula:



15 wherein in each of the above formulae R represents an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion. Specific operable amphoteric detergents include the disodium salt of undecylcyloimidinium-ethoxyethionic acid-2-ethionic acid, dodecyl beta alanine, and the inner salt of 2-trimethylamino lauric acid.

20 The detergent compositions of the invention optionally contain a detergent builder of the type commonly used in detergent formulations. Useful builders include any of the conventional inorganic water-soluble builder salts, such as, for example, water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, silicates, carbonates, and the like. Organic builders include water-soluble phosphonates, polyphosphonates, polyhydroxysulphonates, poly-  
25 acetates, carboxylates, polycarboxylates, succinates and the like.

Specific examples of inorganic phosphate builders include sodium and potassium triphosphates, pyrophosphates and hexametaphosphates. The organic polyphosphonates specifically include, for example, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Examples of these and other phosphorous builder compounds are disclosed in U.S. Patent Nos. 3,213,030; 3,422,021; 3,422,137 and 3,400,176. Pentasodium triphosphosphate and tetrasodium pyrophosphate are especially preferred water-soluble inorganic builders.

Specific examples of non-phosphorous inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali metal, for example, sodium and potassium, carbonates, bicarbonates and silicates are particularly useful herein.

Water-soluble organic builders are also useful. For example, the alkali metal, ammonium and substituted ammonium acetates, carboxylates, polycarboxylates and polyhydroxysulphonates are useful builders for the compositions and processes of the present invention. Specific examples of acetate and polycarboxylate builders include sodium potassium, lithium, ammonium and substituted ammonium salts of ethylene diaminetetracetic acid, nitrilotriacetic acid, benzene polycarboxylic (i.e. penta- and tetra-) acids, carboxymethoxysuccinic acid and citric acid.

Water-insoluble builders may also be used, particularly, the complex silicates and more particularly, the complex sodium alumino silicates such as, zeolites, e.g. zeolite 4A, a type of zeolite molecule wherein the univalent cation is sodium and the pore size is about 4 Angstroms. 45 The preparation of such type of zeolite is described in U.S. Patent 3,114,603. The zeolites may be amorphous or crystalline and have water of hydration as known in the art.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

50 EXAMPLES 1A to 1C

**Example 1A.** This is a comparison example.

Agglomerates of Thixojel No. 1 clay were used in the present example and were prepared by the procedure described below wherein the following components were used: Thixojel No. 1 clay (325 mesh) and an aqueous agglomerating solution containing 7% of sodium silicate having a ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  of about 1:2.4. Thixojel is the tradename of a Wyoming bentonite clay sold by Georgia Kaolin Co., Elizabeth, New Jersey.

The agglomerates were prepared in a rotary drum characterised by a 19.5 inch (49.5 cms) diameter, a 23.5 inch (59.7 cms) length and an axis of rotation adjustable between ten and ninety degrees from the vertical.

9.1 Kg of Thixojel No. 1 clay was charged into the above-described rotary drum which was aligned at an angle of 20 degrees from the vertical. 3.2 Kg of the aqueous silicate solution at a temperature of 43°C was sprayed on to the clay while the drum was rotating at about 6 rpm. The axis of the rotary drum was then adjusted to an angle of 70 degrees from the vertical and an additional 3.2 kg of silicate solution was sprayed on to the clay. The resulting wet agglomerates of clay were transferred in 2 kg portions to an Aeromatic ST-5 (tradename) fluid

bed dryer, manufactured by Aeromatic Corp., Summerville, New Jersey, and dried to approximately 10 wt % moisture using an air flow rate of about 6,000 litres per minute and an air inlet temperature of 71°C. Drying was effected in about 15 minutes. The dried material was then passed through a Stokes granulator having a 40 mesh screen (U.S. Sieve Series) (which has openings 420 microns across), the product particle size being between 40–100 mesh (420–149 microns). The fines passing through a 100 mesh (149 microns) screen were recycled to the rotary drum.

A spray dried granular unperfumed detergent composition was used as a component of the formulation described below and had the following composition:

10				10
	Component	Weight Percent		
	Sodium tridecyl benzene sulphonate	15		
15	Sodium tripolyphosphate	33		15
	Sodium silicate (1Na <sub>2</sub> O: 2.4SiO <sub>2</sub> )	7		
	Sodium carbonate	5		
	Borax	2		
	Sodium sulphate	27.8		
20	Carboxymethyl cellulose	0.2		20
	Moisture	10		

100 grams of the above-described unperfumed detergent composition was blended with 0.2 g of a conventional detergent-type perfume based on limonene, geraniol, citral, cedrol, benzyl acetate, p-t-butyl cyclohexyl acetate and other aromatic ingredients in a Twin-Shell blender for ten minutes at a blender speed of about 20 rpm.

*Example 1B.* This is a comparison example.

80 g of the unperfumed detergent composition described above was blended with 0.2 g of the same perfume employed in Example 1A in accordance with the procedure described above. 19.8 g of agglomerated Thixojel No. 1 as prepared above in Example 1A was then added to the blender and mixed with the contents thereof for about 10 minutes at a blender speed of about 20 rpm.

*Example 1C*

19.8 g of agglomerated Thixojel No. 1 is blended for about 10 minutes with 0.2 g of the same perfume used in the formulations of Examples 1A and 1B in the Twin-Shell blender referred to in Example 1A. The resulting perfume-containing Thixojel clay is then put into a one-litre laboratory model drum which is rotated by a motor at about 10 rpm. Varisoft 3690 is then added dropwise to the clay while the drum is rotating so as to stimulate in the laboratory-scale equipment the effect of spraying the QA compound upon the clay. Varisoft 3690 is methyl(o)-lelyl amido ethyl(2)oleyl imidazolinium-methyl sulphate (75% active ingredients in 25% isopropanol) manufactured by Sherex Chemical Company, Dublin, Ohio. The amount of QA compound added to the particles relative to the weight of clay (based on the active ingredient in the Varisoft 3690) is 0.15 g/10g clay. The resulting agglomerates of clay are then removed from the rotating drum and mixed for about 10 minutes in a blender with 80g of the unperfumed detergent composition described above in Example 1A.

Accordingly, the formulation of Example 1A represents a typical conventional detergent formulation containing perfume; the formulation of Example 1B represents a detergent formulation similar to that of Example 1A but which in addition contains clay agglomerates; and the formulation of Example 1C represents a detergent formulation containing the perfume-containing carrier of the present invention.

Perfume tests are carried out using cotton, Dacron polyester, and Dacron polyester/cotton (65/35) swatches and terry towels which are washed in a conventional U.S. washing machine at 25°C using water having a hardness of 100 ppm as calcium carbonate. Each of three sets of the above-described swatches are separately washed using 100 g of the formulations of Examples 1A, 1B and 1C, a different formulation being used for each washing.

Then the washing procedure is completed, the swatches are evaluated and the fabrics washed in the formulation of Example 1C are found to retain the most perfume fragrance relative to the fabrics washed in the formulations of Examples 1A and 1B.

Based on the above, the use of the perfume-containing carrier of the present invention in a granular detergent composition results in a significant increase in the retention of a perfume fragrance on the laundered fabrics.

### EXAMPLES 2A to 2C

The perfume tests described in Examples 1A to 1C are repeated using 100 g of each of the formulations for each washing as described in the examples except that in the formulation of Example 1C, instead of adding Varisoft 3690 to the perfume-containing Thixojel clay, there is added primary tallow amine.

When the washing procedure is completed, the swatches are evaluated and the fabrics washed in the formulation of Example 1C are found to have a stronger perfume fragrance than the fabrics washed in the formulations of Examples 1B and 1C.

Improved perfume fragrance is achieved when the above-described perfume test is repeated using instead of primary tallow amine, one of the following amines, diamines and diamine salts to coat the Thixojel clay in the formulation of Example 1C: secondary tallow methyl amine (Example 3), tritallow amine (Example 4), N-coco-1,3-diaminopropane (Example 5), N-tallow-1,3-diaminopropane (Example 6) and N-tallow-1,3-diaminopropane diacetate (Example 7).

### 15. CLAIMS

1. A perfume-containing carrier comprising (i) discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume, the said perfume being adsorbed or absorbed or adsorbed and absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of surface active detergent compounds other than cationic detergents.
2. A carrier as claimed in Claim 1 in which the said fabric adhesive agent is a quaternary ammonium compound.
3. A carrier as claimed in Claim 2 in which the said quaternary ammonium compound contains more than eight carbon atoms.
4. A carrier as claimed in Claim 1, 2 or 3 in which the amount of the said quaternary ammonium compound is from about 0.2 to 16%, by weight.
5. A carrier as claimed in Claim 1, 2, 3 or 4 in which the weight of the said fabric adhesive agent is from about 0.2 to less than about 5%, by weight.
6. A carrier as claimed in any one of Claims 1 to 5 in which the weight ratio of the clay mineral and/or zeolite to perfume in the said carrier is from about 10:1 to about 200:1.
7. A carrier as claimed in any one of Claims 1 to 6 in which the weight of perfume is from about 0.2 to about 10%, by weight.
8. A carrier as claimed in any one of Claims 1 to 7 in which the said particles contain a smectite-type clay.
9. A carrier as claimed in any one of Claims 1 to 8 in which the said particles contain a bentonite clay.
10. A carrier as claimed in any one of Claims 1 to 9 in which the said particles contain a zeolite.
11. A carrier as claimed in any one of Claims 1 to 10 in which the said particles contain at least 90%, by weight, of the said clay mineral and/or zeolite.
12. A carrier as claimed in Claim 1 substantially as specifically described herein with reference to Example 1C, 2C or 3 to 7.
13. A particulate laundry detergent composition comprising:
  - (a) from about 0.1 to about 50%, by weight, of a perfume-containing carrier comprising (i) discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of detergent compounds other than cationic detergents;
  - (b) from about 2 to about 50%, by weight, additional to any detergent compound in the said carrier, of one or more surface active detergent compounds selected from the group consisting of anionic, non-ionic, cationic, ampholytic and zwitterionic detergent compounds;
  - (c) from about 0 to about 70%, by weight, of a detergent builder salt; and
  - (d) the balance comprising water and optionally a filler salt.
14. A particulate laundry detergent composition as claimed in Claim 13 in which the perfume containing carrier is as claimed in any one of Claims 1 to 12.

15. A particulate laundry detergent composition as claimed in Claim 13 or Claim 14 in which the said perfume is adsorbed or absorbed or adsorbed and absorbed on the said particles.
16. A particulate laundry detergent composition as claimed in Claim 13, 14 or 15 which additionally contains a second perfume to supplement the fragrance provided by the said perfume-containing carrier. 5
17. A laundry detergent composition as claimed in any one of Claims 13 to 16 in which the said detergent builder salt is present in an amount of from about 5 to about 50%, by weight.
18. A composition as claimed in any one of Claims 13 to 17 in which the amount of fabric adhesive agent is from about 0.05 to about 2%, by weight, of the said detergent composition.
- 10 19. A particulate laundry detergent composition as claimed in Claim 13 substantially as specifically described herein with reference to any one of the examples. 10
20. A process for depositing perfume on fabrics during laundering which comprises contacting the stained and/or soiled fabrics to be laundered with an aqueous solution or dispersion which contains a perfume-containing carrier as claimed in any one of Claims 1 to 12.
- 15 21. A process for depositing perfume on fabrics during laundering which comprises contacting the stained and/or soiled fabrics to be laundered with an aqueous solution or dispersion which contains a particulate laundry detergent composition as claimed in any one of Claims 13 to 19. 15
22. A laundry detergent product comprising:
- 20 (a) agglomerate particles which contain as individual components thereof (i) particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; and (ii) granules of a detergent composition devoid of a soap; each of the said agglomerate particles being comprised of an inner portion and a surface portion, the inner portion of the agglomerate particles being contiguous with and essentially surrounded by the surface portion, 25 the said inner portion consisting essentially of the said granular detergent composition and the said surface portion consisting essentially of the said particles; 25
- (b) a perfume, the said perfume being adsorbed and/or absorbed on the surface portion of the said agglomerate particles; and
- (c) a fabric adhesive agent comprising at least one of an anionic detergent compound, a 30 nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the surface portion of the said agglomerate particles and forming at least a partial coating thereupon. 30
- 35 23. A laundry detergent product as claimed in Claim 22 in which the particles containing at least 75% by weight, of a zeolite or a clay mineral (other than talc) are carrier particles as claimed in any one of Claims 1 to 12. 35
24. A laundry product as claimed in Claim 22 or Claim 23 in which the said granules of detergent composition contain from about 2 to about 50%, by weight, of a surface active 40 detergent compound selected from the group consisting of anionic, nonionic, cationic, amphoteric and zwitterionic detergent compounds. 40
25. A laundry product as claimed in Claim 22, 23 or 24 in which the weight of perfume in the particles is from about 0.2 to about 10%, by weight.
- 45 26. A laundry product as claimed in Claim 22 substantially as specifically described herein with reference to any one of the examples. 45